D. Joining of Advanced Materials by Plastic Deformation

Principal Investigator: J. L. Routbort
Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439-4838
(630) 252-5065; e-mail: routbort@anl.gov

Technology Development Area Specialist: Sidney Diamond
(202) 586-8032; fax: (202) 586-1600; e-mail: sid.diamond@ee.doe.gov
Field Technical Manager: Philip S. Sklad
(865) 574-5069; fax: (865) 576-4963; e-mail: skladps@ornl.gov

Participants:
D. Singh, Argonne National Laboratory
F. Gutierrez-Mora, Argonne National Laboratory
K. C. Goretta, Argonne National Laboratory

Contractor: Argonne National Laboratory
Contract No.: W-31-109-Eng-38

Objectives

- Join advanced materials such as ceramics, cermets, intermetallics, composites, and biomaterials by plastic deformation.
- Collaborate with industry and universities to produce sensors.
- Characterize the interfaces.

Approach

- Apply a modest compressive load to two pieces of similar or dissimilar materials that have had little surface preparation in the temperature region where the materials are known to deform by grain-boundary sliding.
- Examine interfaces by scanning electron microscopy (SEM).
- Measure residual stresses after joining dissimilar materials and compare with finite element analysis.
- Measure strength of the interface by 4-point bend tests.
- Characterize electrical properties of sensors.

Accomplishments

- Made strong, pore-free joints with various ceramics, cermets, intermetallics, composites, and more recently, biomaterials, with and without various interlayers. Fracture occurs away from the interface.
- Achieved joint strength equal to that of the monolithic.
- Filed patent disclosure for producing oxygen sensor.

Future Direction

- Join intermetallics to ceramics.
- Join biomaterials.
- Use functionally graded materials to distribute and reduce interfacial stress concentrations.
- Measure in-situ grain rotation during deformation or joining using the Advanced Photon Source, pending funding.

Introduction

Joining by plastic deformation has been successfully applied in this program to various advanced ceramics: yttria-stabilized zirconia (YSZ)/alumina composites, mullite, silicon carbide and titanium carbide whiskers in a zirconia-toughened alumina (ZTA) matrix, metal-matrix composites and even an electronic ceramic, $La_{0.85}Sr_{0.15}MnO_3$.[1–5] Techniques have been developed to minimize sample preparation procedures and the temperature at which the joining takes place. Among them, a spray application technique[2] or use of nanocrystalline powders or dense interlayers stand out.[2, 6] A patent application is pending. More recently, we have formed pore-free joints in Ni_3Al.

Although it is clear that joining by plastic deformation has few, if any, serious deficiencies for joining similar materials, some issues remain to be addressed when dissimilar materials are to be joined. The situation is different because of the residual stresses generated upon cooling after materials with different coefficients of thermal expansion (CTEs) are joined at the high temperatures required. The thermal residual-stress distribution has been characterized in YSZ-alumina composites by finite element analysis (FEA) simulation and later compared with experimental observation from Vickers indentation measurements.[1]

During FY 2004, we completed the 4-point bend tests on joined pieces of the same and different compositions of YSZ/alumina ceramics that were discussed in the annual report for FY 2003. Fracture mechanics principles, in conjunction with fractographic analysis, are used to explain strengths of joined ceramics in the presence of residual stresses. We have also characterized the high-temperature mechanical properties of hydroyapatite and successfully produced pore-free joints. Collaboration with Ohio State University has resulted in a patent application for an oxygen sensor with a built-in reference.

Summary of 4-Point Bend Tests

Table 1 is a reproduction from the FY 2003 annual report showing the fracture stress of the various monoliths of YSZ/alumina and of the ZT50A/ZT50A joint. The designation is YSZ containing 50% alumina.

Table 1. Flexure data for monolithic ceramics. Al_2O_3 and ZTA from literature

Material	Strength (MPa)
Al_2O_3	300
ZT80A	560 ± 70
ZT60A	580 ± 80
ZT50A	650 ± 100
ZT20A	1020 ± 150
YSZ	1030
ZT50A/ZT50A	620 ± 100

The ZT50A/ZT50A joint fractured, on the average, about 2±1.5 mm from the interface, clearly indicating the strong nature of the joint.

Table 2 presents the results of the flexure test data for dissimilar jointed materials.[7, 8]

Table 2. Flexure data for dissimilarly joined ceramics

Joint	Strength (MPa)	Distance—fracture to interface (μm)
ZT50A/ZT50A	620 ± 100	1950±1540
ZT60A/ZT40A	365 ± 135	335 ± 150
AT60A/ZT40A	500 ± 50	690 ± 110
ZT60A/ZT0A	440 ± 80	380 ± 1008

FEA was conducted to determine the effect of residual stresses generated during joining of dissimilar materials on the mechanical behaviour of joined samples. Figure 1 shows the distribution of normal residual stresses generated as ZT60A joined to ZT20A cools from the joining temperature.[1] A high tensile stress (~250 MPa) perpendicular to the joint interface develops in the material with a lower CTE. In our case, this material corresponds to the composite with a lower YSZ volume fraction (ZT60A), because the CTE of the alumina is considerably lower than that of YSZ.[1] Also, the location of peak residual tensile stress normal to the interface is 150–200 µm away from the physical interface in the ZT60A composite. Moreover, normal stresses parallel to the interface are compressive in the material with lower CTE (ZT60A) and tensile for the material with higher CTE (ZT20A). This high tensile residual stress perpendicular to the interface has an important effect on mechanical performance of the joined dissimilar materials during flexure tests. Similar simulations were also conducted for ZT60A/ZT40A and ZT60A/ZT0A joined samples.

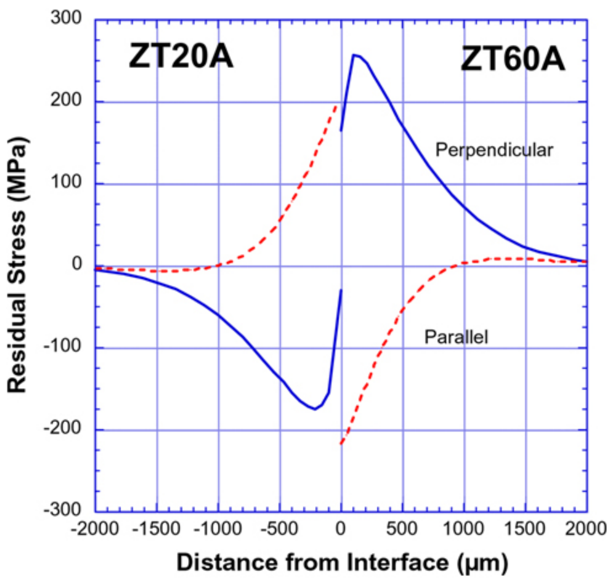

Figure 1. Distribution of residual normal stresses per FEA simulation for a ZT20A/ZT60A joint.

In addition to the normal stresses, shear stresses are also generated, and their variation for ZT60A/ZT0A joined samples determined by FEA is shown in Figure 2. Shear stresses are developed close to the interface; they fall off rapidly within a short distance from the interface. The magnitude of shear stresses is small compared with the normal tensile stresses. Thus it is expected that failure

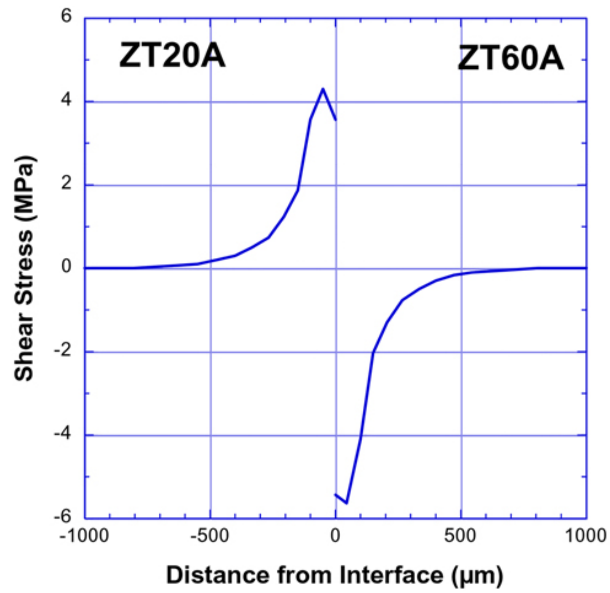

Figure 2. Distribution of residual surface shear stresses per FEA simulation for a ZT20A/ZT60A joint.

will be controlled by the normal tensile stresses of these joined samples.

Several key inferences can be drawn from the results of dissimilar joined samples. First, all samples failed in the ZT60A portion, the lower-strength material with tensile stresses normal to the interface. Second, for ZT60A joined to ZT20A and ZT0A, the strength of joined samples decreased as the difference in composition between the parts joined or the CTE mismatch increased. For the experiment in which there was the largest difference in composition (YSZ joined to ZT60A), flexure strength decreased by 25% compared with the strength of monolithic ZT60A. However, strengths for ZT60A/ZT40A joined samples showed lower mean strength and large scatter compared with joined samples of ZT60A/ZT20A and ZT60A/ZT0A. Reasons for this will be discussed. Third, for all the dissimilar joints, failure was found to be away from the interface, again confirming the strong interface and efficacy of the joining process for materials with dissimilar compositions and CTEs.

The decreased strength of ZT60A when joined to compositions with a lower volume fraction of alumina, compared with the strength of ZT60A, can be attributed to the presence of tensile residual stresses and the location and size of the failure-causing flaw. It is expected that the reduction in strength in the joined sample will depend on the region of near-maximum tensile residual stresses. In this regard, the distance from the interface at which fracture occurred is especially revealing. For the ZT60A/ZT20A joint sample, the average failure location is about 700 μm away from the interface in the ZT60A section (Table 2). This corresponds to about 100 MPa tensile residual stress as per FEA simulations, as shown in Figure 1. By simple superposition of the residual stress intensities on the applied stress intensity during flexure tests, the failure strength for ZT60A should be reduced by 100 MPa. This is in agreement with the reduction of approximately 80 MPa in flexural strength of ZT60A when joined to ZT20A. Similar correlations between residual tensile stresses and flexural strength for ZT60A/ZT0A have been made.

Strengths of ZT60A/ZT40A were somewhat lower and were 201, 360, and 530 MPa for the three joined samples tested. Close inspections of the fracture sites were made for all samples. The lower strengths of 360 and 201 MPa observed for the two samples is believed to be due to the presence of larger flaws. To confirm this, fractography was conducted on the two low-strength samples. SEM photomicrographs revealed surface damage on the tensile surfaces in the two low-strength samples. It is speculated that this damage was introduced during the sample preparation steps or handling. Typical lengths of this damage were 70–90 μm. Using a nominal crack length of 80 μm, apparent toughness of 3.6 $MPam^{1/2}$ for ZT60A, and fundamental fracture mechanics,[9] the fracture strength was calculated to be approximately 350 MPa. This calculated fracture strength is consistent with the measured strength for the low-strength ZT60A/ZT40A sample. Thus, in addition to the residual stresses, the size and distribution of failure-causing flaws in the ceramic materials will control the strength of the joint. This also explains why failure location in the joined samples does not necessarily coincide with the peak tensile residual stresses.

Design and Fabrication of Air- Reference Free Potentiometric Planar

A realistic miniaturization of a high-temperature, potentiometric planar oxygen sensor is possible by replacing the open-air reference column in current sensors with a metal/metal oxide Rhines pack at high temperatures. Gas-tight sealing of the internal reference oxygen pressure was a problem, but eventually perfect seals were obtained by joining the edges of the ceramic components by plastic deformation. This design, free of external reference,enables position flexibility and mobility of the sensor inside all combustion units. This report will detail the work that was performed in conjunction with a team from Ohio State University after it contacted ANL and detailed the sealing problems they were encountering using more conventional methods.

The main components for the sensor fabrication are made of yttria-doped tetragonal zirconia polycrystalline (YTZP) ceramics, pellets, a ring, and green tapes. One YTZP pellet is partly covered with platinum ink, and a small-gauge platinum (Pt) wire is placed within intimate contact of the Pt ink in order to create a reference electrode. This electrode ink on the pellet (electrolyte) is fired at 1000°C in order to cure the electrode ink. The Pt wire is slipped between two rings of TYZP green tapes, and the pellet is placed wire-down onto the other fabrication components as shown in Figure 3. The components are joined together in a two-step process. The first joining step produces a cylinder, after which Ni/NiO powder is inserted into the cylinder and lightly compacted. Finally, the tapes and electrodes with the Pt wire are joined to the filled cylinder. Joining was readily achieved at 1200°C in an argon atmosphere using a nominal strain rate of $4 \times 10^{-5}\ s^{-1}$.

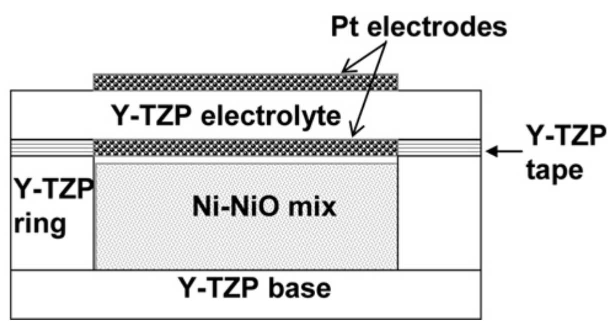

Figure 3. Ceramic components and stacking of the internal reference planar oxygen sensor.

An SEM micrograph of the top joint (with tapes) is shown in Figure 4. The sharply delineated edges of the joint shown in the low-magnification micrograph are the result of a slight offset between

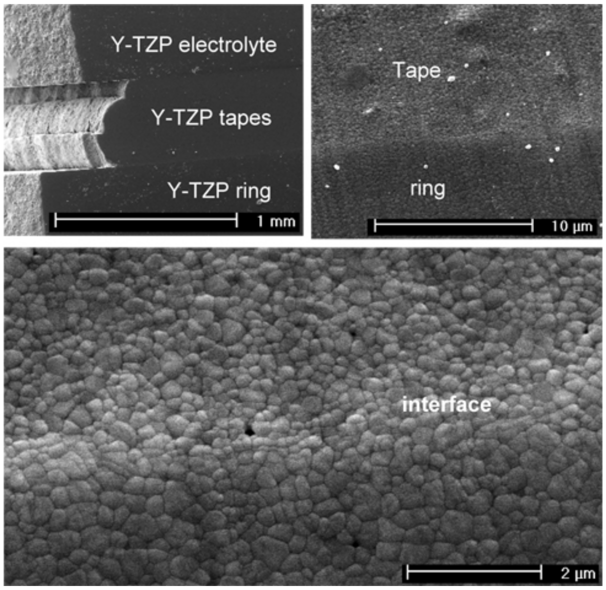

Figure 4. Top joint microstructure (with tapes).

the top disk, the green tapes, and the cylinder. However, it can be seen that the joint contains only a very limited amount of porosity that was present in the initial materials.

The electromotive force (EMF) as a function of oxygen partial pressure at 600°C is shown in Figure 5. These tests, performed as a function of time, indicate that the joints are indeed gas tight.

Summary of Sensor Production

The plastic joining technique works and produces gas-tight seals. The sensor is viable and has the required sensitivity and response time. However, the EMF does not agree with the theoretical calculated EMF. This is most likely because the Ni/NiO was reduced by joining at 1200°C in an argon atmosphere. In the coming fiscal year, experiments will be performed to produce sensors joined in air or even in pure oxygen. Furthermore, several candidate reference materials under consideration may yield higher sensitivities. This work will form part of the Ph.D. thesis of John Spirig.

Joining of Hydroxyapatite

Hydroxyapatite (HA) is a very common biomaterial that is generally used as a coating over a non-biocompatible material for implants such as teeth. Of course, coatings can be inexpensively applied using a number of different techniques.

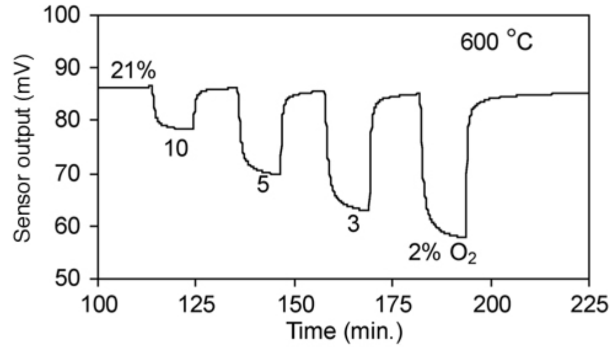

Figure 5. Oxygen sensing response at 600 °C of the fabricated sensor. Sensor has been gas-tight for several months.

However, producing complex shapes by these techniques is difficult. Joining by plastic deformation presents a new possibility for production of complex pieces of HA. Therefore, the first phase of this work was to determine the conditions under which HA exhibits plasticity.

HA was obtained from Professor Eldon Case of Michigan State University. The material was > 98% of theoretical density and had a bimodal grain size distribution with the largest grains being ≈ 5 µm and the smallest ≈ 1 µm. Figure 6 indicates that HA deforms into nearly a steady-state stress between 2.0 and 2.5 MPa at 1275°C at a strain rate of 10^{-5} s^{-1}. Strains of over 0.08 were achieved without fracture.

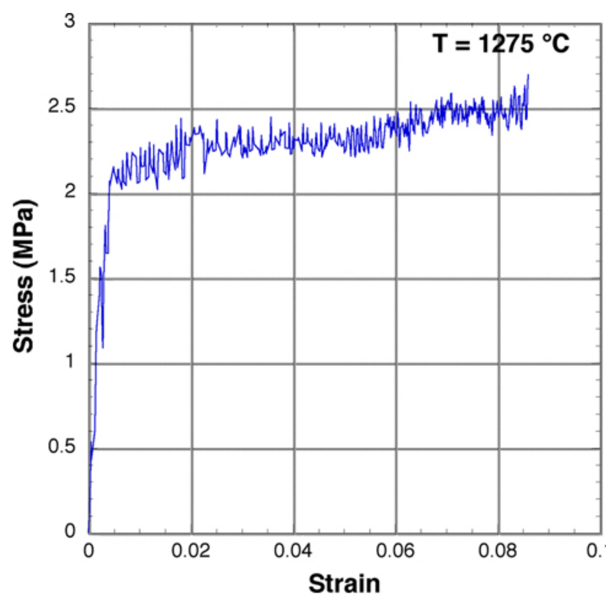

Figure 6. Stress–strain data obtained from hydroxyapatite at 1275°C at a strain rate of 10^{-5} s^{-1}.

Two pieces of HA were placed in the Instron and compressed to about 8% strain at 1275°C using a strain rate of 10^{-5} s^{-1}. The pore–free joint that was produced is shown in Figure 7. The joint is indistinguishable from the matrix. It is also noteworthy that the microstructure was unchanged. The next step will be to determine the temperature, strain, and strain rate region over which joining by plastic deformation is possible.

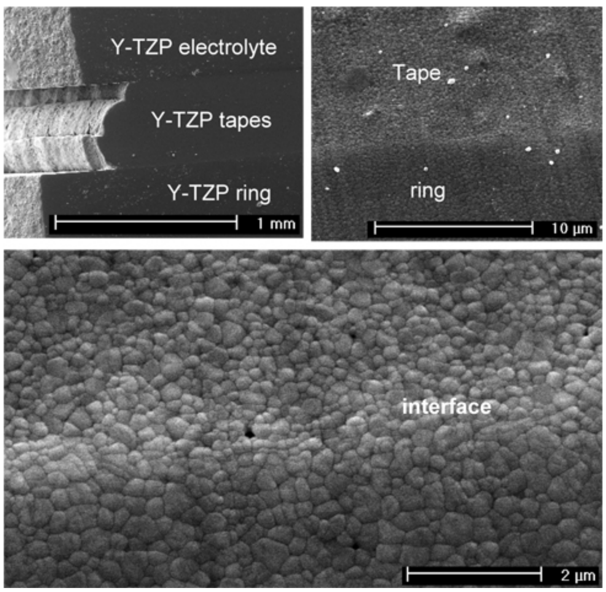

Figure 7. Joint in hydroxapatite produced at 1275°C at a strain rate of 10^{-5} s^{-1}. Arrows indicate the interface between the two joined pieces.

Conclusions

We have shown that we can form pore-free, very strong joints in a wide variety of important materials by plasticity. Previously we have reported on joining structural and electronic ceramics, metal-matrix composites, Ni_3Al, whisker-reinforced ceramics, and cermets. Previous work has shown that experimental determinations of the residual stress agree with calculated values. Little surface preparation and modest temperatures are required for deformation joining. Those factors make the process attractive for commercialization. Using the alumina/ zirconia system as a model material, we have shown that the fracture of a joined bar of the same composition has the same strength as the matrix. The fracture of a joined 4-pt bend bar of dissimilar compositions does not fracture at the interface, but at a position near the maximum residual tensile stress.

We have continued to expand the materials that can be joined by plastic deformation. In this fiscal year, we have studied high-temperature deformation and joined a biomaterial, HA. We have applied the technique to a practical problem, producing a gas-tight oxygen sensor.

Future work will concentrate on joining dissimilar materials, such as intermetallics, to ceramics. We also plan to join optical materials and assess the quality of the join using optical transmission. Preliminary feasibility studies to perform an in-situ deformation study of grain rotation are under way. We are investigating the deformation characteristics of several possible candidate materials with a view of choosing one that has suitable X-ray transmission properties, but that deforms into steady state at modest temperatures by grain boundary sliding. Preliminary designs of a furnace and deformation apparatus will be considered in FY 2005, pending funding.

References

1. F. Gutiérrez-Mora, K. C. Goretta, S. Majumdar, J. L. Routbort, M. Grimdisch, and A. Domínguez-Rodríguez, "Influence of Internal Stresses in Superplastic Joining of Zirconia Toughened Alumina," *Acta Materialia*, **50,** 3475–3486 (2002).

2. K. C. Goretta, F. Gutiérrez-Mora, J. J. Picciolo, and J. L. Routbort, "Joining Alumina/Zirconia Ceramics," *Mat. Sci. and Eng.*, **A341,** 158–162 (2003).

3. F. Gutierrez-Mora, K. C. Goretta, J. L. Routbort, and A. Dominguez-Rodriguez, "Joining of Ceramics by Superplastic Flow," in *Advances in Ceramic Matrix Composites VII, Ceramic Transaction # 128*, ed. N. P. Bansal, J. P. Singh, and H. T. Lin, p. 251, The American Ceramic Society, Westerville, Ohio (2002).

4. N. Chen, F. Gutierrez-Mora, R. E. Koritala, K. C. Goretta, J. L. Routbort, and J. Pan, "Joining Particulate and Whisker Ceramic Composites by Plastic Flow," *Comp. Struct.*, **57,** 135–139 (2002).

5. F. Gutierrez-Mora and J. L. Routbort, "Electrical Characterization of a Joined Electroceramics $La_{0.85}Sr_{0.15}MnO_3$, " *J. Am. Ceram. Soc.*, **85**(9), 2370–2372 (2002).

6. F. Gutiérrez-Mora, A. Domínguez-Rodríguez, J. L. Routbort, R. Chaim and F. Guiberteau, "Joining of Yttria-Tetragonal Stabi-

lized Zirconia Polycrystals using Nanocrystals," *Scripta Mat*. **41,** 455–460 (1999).

7. F. Gutierrez-Mora, D. Singh, N. Chen, K. C. Goretta, J. L. Routbort, and A. Dominguez-Rodriguez, submitted to *J. European Ceramic Society.*

8. F. Gutierrez-Mora, K. C. Goretta, N. Chen, and J. L. Routbort, "Joining of Advanced Ceramics by Plastic Flow," *Ceramics Intl*. **30**, 1945–1948 (2005).

9. H. L. Ewalds and R. J. H. Wanhill, *Fracture Mechanics*, p. 37, Edward Arnold, Delftse, The Netherlands (1984).

Publications and Presentations

A. Dominguez-Rodriguez, F. Gutierrez-Mora, M. Jimenez-Melendo, J. L. Routbort, and R. Chaim, "Current Understanding of Deformation of Y–TZP and Superplastic Joining of Ceramics," *J. Mater. Engr*. **A302**, 154–161 (2001).

A. Dominguez-Rodriguez, F. Gutierrez-Mora, M. Jimenez-Melendo, R. Chaim, and J. L. Routbort, "Superplasticity and Joining of Zirconia–Based Ceramics," presented at the Materials Research Society Symposium, Proceeding 601 99-104, 2000.

F. Gutierrez-Mora, K. C. Goretta, J. L. Routbort and A. Domínguez-Rodríguez, "Joining Ceramics by Superplastic Flow," *Ceramic Transactions* **128**, 252–258 (2002).

K. C. Goretta, F. Gutierrez-Mora, J. J. Picciolo, and J. L. Routbort, "Joining Alumina/Zirconia Ceramics," *J. Mater. Engr*. **A341**, 158–162 (2003).

A. R. De Arellano-Lopez, U. Balachandran, K. C. Goretta, B. Ma, and J. L. Routbort, "High-Temperature Deformation of $Sr(FeCo)_{1.5}O_x$ Ceramics," *Acta Materialia* **49**, 3109–3116 (2001).

F. Gutierrez-Mora, K. C. Goretta, S. Majumdar, J. L. Routbort, M. Grimdisch, and A. Dominquez-Rodriguez, "Influence of Internal Stresses on Superplastic Joining of Zirconia-toughened Alumina," *Acta Materialia* **50**, 3475–3486 (2002).

E. Wuchina, M. Opeka, F. Gutierrez-Mora, R. Koritala, K. C. Goretta, and J. L. Routbort, "Processing and Mechanical Properties of Solid-solutions of Hf-N," *J. European Ceramic Soc*. **22**, 2571–2576 (2002).

N. Chen, F. Gutierrez-Mora, R. E. Koritala, K. C. Goretta, J. L. Routbort, and J. Pan, "Joining Particulate and Whisker Ceramic Composites by Plastic Flow," *Composite Structures*, **57**, 135–139 (2002).

A. R. de Arellano-Lopez, J. J. Melendez-Martinez, A. Dominguez-Rodriguez, T. A. Cruse, R. Koritala, J. L. Routbort, and K. C. Goretta, "Compressive Creep of Mullite Containing Y2O3," *Acta Materialia* **50**, 4325–4338 (2002).

F. Gutierrez-Mora and J. L. Routbort, "Electrical Characterization of a Joined Electroceramic, La0.85Sr0.15MnO3," *J. American Ceramic Society* **85**, 2370–2372 (2002).

F. Gutierrez-Mora, J. M. Ralph, and J. L. Routbort, "High-temperature Mechanical Properties of Anode-Supported Bilayers," *Solid State Ionics* **149**, 177–184 (2002).

A. R de Arellano-Lopez, K. C. Goretta, E. T. Park, S. E. Dorris, U. Balchandran, and J. L. Routbort, "High-temperature Deformation of a BaCe0.8Y0.2O 3-y + Ni Composite," *J. European Ceramic Society* **22**, 2555-2560 (2002).

J. L. Routbort, J. Ralph, R. E. Cook, C. Clauss, and A. R. de Arellano-López, "Creep of (La0.55Sr0.45)0.99Mn1-yGayO3," *Phys. Chem. Chem. Phys*. **5**, 2232–2236 (2003).

K. C. Goretta, F. Gutierrez-Mora, N. Chen, J. L. Routbort, T. A. Orlova, B. I Smirnov, and A. R. de Arellano-López, "Solid-Particle Erosion and Strength Degradation of Si3N4/BN Fibrous Monoliths," *Wear* 256, 233–242 (2004).

J. Martinez-Fernandez, A. R. de Arellano-Lopez, F. M. Varela-Feria, T. S. Orlova, K. C. Goretta, F. Gutierrez-Mora, Nan Chen, and J. L. Routbort, "Erosion and Strength Degradation of Biomorphic SiC," *J. European Ceramic Society* **24**, 861–870 (2004).

K. C. Goretta, Nan Chen, F. Gutierrez-Mora, J. L. Routbort, G. C. Lukey, and J. S. J. van Deventer, "Solid-Particle Erosion of a Geopolymer Containing Fly Ash and Blast-Furnace Slag," *Wear* **256**, 714–719 (2004).

F. Gutierrez-Mora, K. C. Goretta, Nan Chen, and J. L. Routbort, "Joining of Advanced Ceramics by Plastic Flow," *Ceramics International* **30**, 1945–1948 (2004).

F. Gutierrez-Mora, D. Singh, N. Chen, K. C Goretta, J. L. Routbort, and A. Dominguez-Rodriguez, "Fracture of Composite Alumina/Yttria-stabilized Joints," *J. European Ceramic Society*, in press

K. C. Goretta, T. A. Cruse, D. Singh, J. L. Routbort, A. R. de Arellano-Lopez, T. S. Orlova, and B. I. Smirnov, "Ceramic Fibrous Monolithic Structures," *Composite Structures* **66**, 547–553 (2004).

D. Singh, F. Guiterrez-Mora, N. Chen, K. C. Goretta, and J. L. Routbort, "Joining of Advanced Structural Materials by Plastic Deformation," *Advances in Ceramics*, in press.

F. Guiterrez-Mora, K. C. Goretta, D. Singh, J. L. Routbort, S. Sambasivan and K. Steiner, "High-Temperature Mechanical Behavior of Aluminum-Phosphate Based Glass Ceramics (Cerablak)," *J. European Ceramic Society*, in press.

Patent Applications

K. C. Goretta, J. L Routbort, and F. Gutiérrez-Mora, "Joining of Advanced Materials by Plastic Deformation, invention report, 0003/00950.

J. L. Routbort, et al., "Method Of Fabrication of a High-Temperature Potentiometric Oxygen Sensor," invention report ANL-IN-04-105